



PL-DEAM, A Versatile Resin for Boronic Acids

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Introduction

PL-DEAM Resin is a versatile resin designed for use with boronic acids. Boronic acids are widely used in organic synthesis, particularly in Suzuki coupling reactions

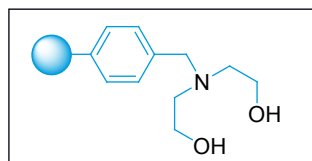


Figure 1. PL-DEAM Resin structure

– a key carbon-carbon bond forming reaction. PL-DEAM Resin is dual-purpose. It can be used as a scavenger resin to remove excess boronic acids from non-aqueous solutions [1], or to immobilize boronic acids for further functionalization [2,3]. A variety of commercially available boronic acids of the general formula $R-B(OH)_2$ can be attached to the resin, enabling modification of the side chain group R. This allows the creation of novel boronic acids to further increase the diversity in organic synthesis [4]. The products are readily cleaved from the resin using an aqueous acid/THF mixture. Alternatively, the Suzuki reaction can be carried out with the polymer bound boronic acid itself – ideal for producing biphenyl derivatives through reaction with iodobenzene compounds [5]. PL-DEAM MP-Resin can be used for boronic acid immobilization in polar protic solvents and is also a highly effective scavenger of metals from solution, in particular platinum and tin species.

Description

Polymer supported diethanolamine

Solvent compatibility – microporous

Toluene, DMF, THF, DCM, DCE, NMP, Dioxane

Solvent compatibility – macroporous

Toluene, DMF, THF, DCM, DCE, NMP, Dioxane, MeOH, EtOH, H_2O

Applications

Scavenging of boronic acids from a Suzuki-Miyaura reaction

To a (5:1) ethanol: 2 M aq K_2CO_3 solution, add aryl bromide or iodide (1.0 eq) and boronic acid (1.5 eq). Purge the reaction under a blanket of argon and add 10 mol percentage of a suitable palladium catalyst. At the end of the reaction the excess boronic acid can be effectively removed from the reaction mixture using PL-DEAM Resin, (2 eq) at room temperature for 2-12 hours. Some boronic acids may be scavenged more quickly than others. The HPLC run (A) shows a crude Suzuki reaction mixture with excess boronic acid and desired biaryl product. The HPLC run (B) shows that the boronic acid has been effectively scavenged.

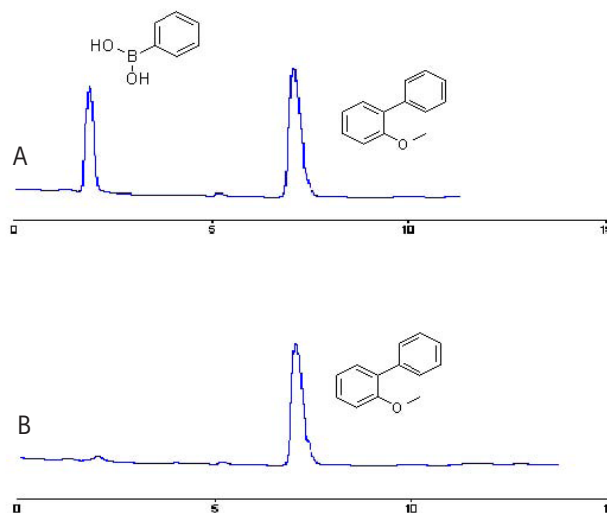


Figure 3. HPLC trace of a Suzuki-Miyaura reaction containing excess boronic acid (A) and post treatment with PL-DEAM Resin (B).

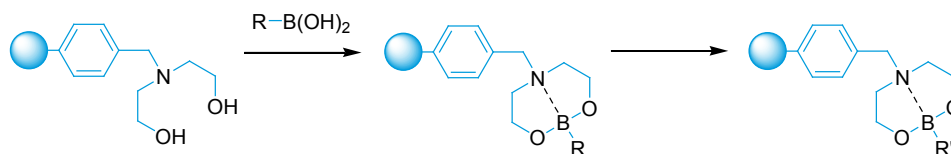


Figure 2. The modification and subsequent cleavage of an immobilized boronic acid using PL-DEAM Resin.

Immobilization of boronic acids to PL-DEAM Resin

Dissolve the boronic acid (1.2 eq) in anhydrous tetrahydrofuran (THF). Then add PL-DEAM Resin (1 eq) and agitate for 1–3 hours. For larger scale applications, the solution should be cooled to 0 °C prior to the resin being added. After the reaction is complete, wash with anhydrous THF to remove any unchelated boronic acid. Subsequent reactions should be performed under anhydrous conditions.

Cleavage of boronic acids from PL-DEAM Resin

The boronic acid can be easily cleaved from the resin using a solution of THF/water/acetic acid (90:5:5). The cleavage reaction should take 1–2 hours. After this time, remove the resin by filtration and wash the beads with more THF. The combined washings may then be evaporated to yield the desired boronic acid.

Metal scavenging applications of PL-DEAM MP-Resin

PL-DEAM MP-Resin can be used for boronic acid immobilization in polar protic solvents and is also a highly effective scavenger of metals from solution, in particular platinum and tin species. Table 1 shows the residual metal concentration of various metals when a 1000 ppm solution of each metal has been scavenged by PL-DEAM MP-Resin. (Reactions were run in water).

Table 1. Residual metal concentration of various metals.

Metal	Residual Concentration (ppm)
Ruthenium	44.8
Lead	34.1
Palladium	10.4
Platinum	4.5
Tin	3.1

References

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These data represent typical results.

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